

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of Eiju SUZUKI, et al.

Application No.: 10/562,157

Filed: December 23, 2005

For: BUTADIENE-BASED POLYMER AND METHOD OF PRODUCING THE SAME AS WELL AS RUBBER COMPOSITION AND TIRE USING THE SAME

Group Art Unit: 1796

Examiner: Fred M. Teskin

Confirmation No.: 6585

DECLARATION UNDER 37 C.F.R. § 1.132

I, Eiju Suzuki, declare that:

I am one of the inventors of the above-captioned patent application.

I received my Master of Science and Technology from Keio University in 1998, I was employed by Bridgestone Corporation from 2002 to 2005, and I have been employed by Bridgestone Americas Center for Research and Technology since 2005, where I have been engaged mainly in research and development of polymers.

I have made the following experiments in order to confirm that US 4,429,089 (Pedretti et al.) does not disclose or suggest a butadiene-based polymer having a 1,3-butadiene monomer unit, characterized in that a cis-1,4 bond content and a vinyl bond content in the 1,3-butadiene monomer unit as measured by a Fourier transform infrared spectroscopy (FT-IR) and calculated according to the following equations (IV) and (VI) are not less than 98.0% and not more than 0.3%, respectively, and a ratio (Mw/Mn) of weight average molecular weight (Mw) to number average molecular weight (Mn) is 1.6-3.5,

$$(\text{cis-1,4 bond content}) = e/(e+f+g) \times 100 (\%) \quad \dots (IV)$$

$$(\text{vinyl bond content}) = g/(e+f+g) \times 100 (\%) \quad \dots (VI)$$

wherein e, f and g are derived from the following matrix (III):

$$\begin{bmatrix} 1.7455 & 0 & -0.0151 \\ -0.0454 & 0.4292 & -0.0129 \\ -0.007 & 0 & 0.3746 \end{bmatrix} \begin{bmatrix} \log_{10}(a/d) \\ \log_{10}(a/b) \\ \log_{10}(a/c) \end{bmatrix} = \begin{bmatrix} e \\ f \\ g \end{bmatrix} \quad \dots (III)$$

wherein a represents a mountain peak value near 1130 cm<sup>-1</sup>, b represents a valley peak

value near  $967\text{ cm}^{-1}$ , c represents a valley peak value near  $911\text{ cm}^{-1}$  and d represents a valley peak value near  $736\text{ cm}^{-1}$  in the FT-IR spectrum.

#### Experimental Procedure

##### Example 36 (Run numbers 2669-143-1, 2669-143-2 and 2669-143-3)

In order to confirm repeatability, the following experiment is repeated three times.

4.0 mg of  $\text{Nd}(\text{O}i\text{Pr})_3$  (STREM cat# 93-6012) is weighted and charged into 150 mL glass bottle fully dried, and sealed with a perforated cap having a rubber plug in a glove box. Then, the glass bottle is removed from the glove box. 50 mL of dried and degassed hexane, 0.74 mL of 0.68 M triisobutylaluminum (TIBA) in hexane and 2.32 mL of 0.025 M aluminum bromide in hexane are sequentially added into this glass bottle and fully stirred to obtain a homogeneous solution. A calculated Nd/TIBA/Br ratio in this catalyst solution is 1/10/3.48.

Then, 45.7 g of 21.9 wt% 1,3-butadiene in hexane is charged into this glass bottle and stirred in a water bath at  $30^\circ\text{C}$  to carry out a polymerization reaction. After two-hour polymerization reaction, 2-propanol containing a small amount of 2,6-di-*t*-butyl paracresol (BHT) is added to stop the polymerization reaction. A polymerization cement in the glass bottle is collected and dried according to a common method to obtain Polymers A, B and C.

##### Preparation of $\text{Nd}(\text{OnBu})_3$ catalyst

968 mg of  $\text{Nd}[\text{N}(\text{TMS})_2]_3$  (Aldrich cat# 547794) is weighted and charged into 100 mL glass flask fully dried, having a ground glass stopper and provided with a stirrer bar made of Teflon, and the glass flask is sealed with the ground glass stopper in a glove box. Then, the glass flask is removed from the glove box. 50 mL of dried and degassed benzene is added to this glass flask and stirred with a magnetic stirrer with flowing a dried nitrogen through the flask to obtain a homogeneous blue solution. To this solution is added dropwise 3.5 mL of 1-butanol (Aldrich cat# 281549). Immediately, a color of the solution turns light and a bubble which I believe is  $\text{NH}_3$  as a by-product is observed. The resulting mixture is further stirred at  $50^\circ\text{C}$  in an oil bath with heating. The solution turns blue again as a reaction progresses. After three-hour stirring, all solvent is removed with heating at normal pressure under a dried nitrogen flow to obtain a blue solid. The solid is further dried under reduced pressure. An ICP analysis reveals that the resulting solid has a Nd content of 39.2 wt%.

280 mg of the resulting blue solid is weighted and charged into 150 mL glass bottle fully dried, and sealed with a perforated cap having a rubber plug in a glove box. Then, the glass bottle is removed from the glove box. 30 mL of dried and degassed hexane is added to the glass bottle, and the bottle is irradiated with ultrasonic wave for three hours to obtain a blue suspended solution. A calculated Nd concentration in this solution is 0.0257 M.

Example 26 (Run numbers 2669-161-1 and 2669-161-2)

Two 750 mL glass bottles fully dried are sealed with a perforated cap having a rubber plug respectively, and then a gas in the bottle is substituted by flowing a dried nitrogen through the bottle. 0.53 mL of 0.68 M triisobutylaluminum (TIBA) in hexane, 132 g of 21.5 wt% 1,3-butadiene in hexane, 0.70 mL of the Nd catalyst solution as prepared above and 0.72 mL of 0.050 M ethyl aluminum dichloride in hexane are sequentially charged into these glass bottles respectively. A calculated Nd/TIBA/Cl ratio in this catalyst composition is 1/20/4. The resulting mixture is stirred in a water bath at 20°C to carry out a polymerization reaction. After four-hour polymerization reaction described in the Example of US 4,429,089 (Pedretti et al.), 2-propanol containing a small amount of 2,6-di-t-butyl paracresol (BHT) is added to one glass bottle to stop the polymerization reaction. After a solvent in the glass bottle is removed under a dried nitrogen flow, a polymer cannot be obtained. Also, another glass bottle is continuously stirred for 68 hours in total, the polymerization reaction is stopped and the solvent is removed as in the same manner, but a polymer cannot be also obtained.

Example 29 (Run numbers 2669-167-1 and 2669-167-2)

Two 750 mL glass bottles fully dried are sealed with a perforated cap having a rubber plug respectively, and then a gas in the bottle is substituted by flowing a dried nitrogen through the bottle. 1.96 mL of 0.68 M triisobutylaluminum (TIBA) in hexane, 187 g of 21.5 wt% 1,3-butadiene in hexane, 1.48 mL of the Nd catalyst solution as prepared above and 1.52 mL of 0.050 M ethyl aluminum dichloride in hexane are sequentially charged into these glass bottles respectively. A calculated Nd/TIBA/Cl ratio in this catalyst composition is 1/35/4. The resulting mixture is stirred in a water bath at 40°C to carry out a polymerization reaction. After 1.5-hour polymerization reaction described in the Example of US 4,429,089 (Pedretti et al.), 2-propanol containing a small amount of 2,6-di-t-butyl paracresol (BHT) is added to one glass bottle to stop the polymerization reaction. A solvent in the glass bottle is removed under a dried nitrogen flow, and the resulting polymer is further dried at 60°C in a vacuum drying oven for two hours to obtain 0.26 g of a Polymer D. Also, another glass bottle is continuously stirred for 18 hours in total, the polymerization reaction is stopped and the solvent is removed as in the same manner to obtain 5.57 g of a Polymer E.

Example 40 (Run numbers 2669-171-1 and 2669-171-2)

Two 750 mL glass bottles fully dried are sealed with a perforated cap having a rubber plug respectively, and then a gas in the bottle is substituted by flowing a dried nitrogen through the bottle. 258 g of dried and degassed hexane, 1.55 mL of 0.68 M triisobutylaluminum

(TIBA) in hexane, 3.74 mL of the Nd catalyst solution as prepared above, 1.29 mL of 0.050 M ethyl aluminum dichloride in hexane and 90.7 g of 21.5 wt% 1,3-butadiene in hexane are sequentially charged into these glass bottles respectively. A calculated Nd/TIBA/Cl ratio in this catalyst composition is 1/11/1.34. The resulting mixture is stirred in a water bath at 25°C to carry out a polymerization reaction. After three-hour polymerization reaction described in the Example of US 4,429,089 (Pedretti et al.), 2-propanol containing a small amount of 2,6-di-*t*-butyl paracresol (BHT) is added to one glass bottle to stop the polymerization reaction. A solvent in the glass bottle is removed under a dried nitrogen flow, and the resulting polymer is further dried at 60°C in a vacuum drying oven for two hours to obtain 1.01 g of a Polymer F. Also, another glass bottle is continuously stirred for 20 hours in total, the polymerization reaction is stopped and the solvent is removed as in the same manner to obtain 7.30 g of a Polymer G.

#### Nd(OnC<sub>10</sub>H<sub>21</sub>)<sub>3</sub> catalyst for Examples 18, 19, 21, 23-25, 30-32 and 34

Preparation method or distributor of Nd(OnC<sub>10</sub>H<sub>21</sub>)<sub>3</sub>, required for the Examples 18, 19, 21, 23-25, 30-32 and 34, is not disclosed in US 4,429,089 (Pedretti et al.). Also no search information about Nd(OnC<sub>10</sub>H<sub>21</sub>)<sub>3</sub> is found at CAPLUS with the following search queries; "s neodmium(jdecaoxide)", "s neodmium(jdecanolate)" and "e c30h63NdO3 /mf".

Thus, same procedure for Nd(OnBu)<sub>3</sub> catalyst is applied by using 1-decanol (Aldrich cat# 239763) instead of 1-butanol. After three-hour reaction at 50°C, most part of benzene is removed with heating at normal pressure under a dried nitrogen flow to obtain a greenish blue thick suspension. Further purification to remove residual 1-decanol and byproduct (nC<sub>10</sub>H<sub>21</sub>OTMS) is attempted under vacuum condition (0.8mmHg) by raising temperature to 200°C gradually. A color of the thick suspension turns greenish blue to brownish green as raising temperature. All liquid contents cannot be removed completely even after this degradation.

As seen from this result, disclosed information in US 4,429,089 (Pedretti et al.) is insufficient to produce the Examples 18, 19, 21, 23-25, 30-32 and 34 which require Nd(OnC<sub>10</sub>H<sub>21</sub>)<sub>3</sub> catalyst.

#### - Results

With respect to the resulting Polymers A, B, C, E and G, a *cis*-1,4 bond content, a *trans*-1,4 bond content, a vinyl bond content in the 1,3-butadiene monomer unit are measured by a Fourier transform infrared spectroscopy (FT-IR), and further a weight average molecular weight (Mw) and a number average molecular weight (Mn) are measured to determine a ratio (Mw/Mn) of weight average molecular weight (Mw) to number average molecular weight (Mn). Results are shown in the following table.

Table

Run No.	2669-143-1	2669-143-2	2669-143-3	2669-161-1	2669-161-2	2669-167-1	2669-167-2	2669-171-1	2669-171-2
Example No.	36	36	36	26	26	29 (1/10 scale)	29 (1/10 scale)	40 (1/20 scale)	40 (1/20 scale)
Component C (mmol)	Nd(OiPr) <sub>3</sub> 0.05	Nd(OiPr) <sub>3</sub> 0.05	Nd(OiPr) <sub>3</sub> 0.05	Nd(OnBu) <sub>3</sub> 0.018	Nd(OnBu) <sub>3</sub> 0.018	Nd(OnBu) <sub>3</sub> 0.038	Nd(OnBu) <sub>3</sub> 0.038	Nd(OnBu) <sub>3</sub> 0.096	Nd(OnBu) <sub>3</sub> 0.096
Component A (mmol)	Al(iBu) <sub>3</sub> 0.5	Al(iBu) <sub>3</sub> 0.5	Al(iBu) <sub>3</sub> 0.5	Al(iBu) <sub>3</sub> 0.36	Al(iBu) <sub>3</sub> 0.36	Al(iBu) <sub>3</sub> 1.33	Al(iBu) <sub>3</sub> 1.33	Al(iBu) <sub>3</sub> 1.06	Al(iBu) <sub>3</sub> 1.06
Component B (mmol)	AlBr <sub>3</sub> 0.058	AlBr <sub>3</sub> 0.058	AlBr <sub>3</sub> 0.058	EtAlCl <sub>2</sub> 0.036	EtAlCl <sub>2</sub> 0.036	EtAlCl <sub>2</sub> 0.076	EtAlCl <sub>2</sub> 0.076	EtAlCl <sub>2</sub> 0.064	EtAlCl <sub>2</sub> 0.064
1,3-butadiene (g)	10.0	10.0	10.0	28.4	28.4	40.2	40.2	19.5	19.5
Polymerization condition	30°C, 2 hrs	30°C, 2 hrs	30°C, 2 hrs	20°C, 4 hrs	20°C, 68 hrs	40°C, 1.5 hrs	40°C, 18 hrs	25°C, 3 hrs	25°C, 20 hrs
Yield (%)	66.7	70.5	69.8	0	0	0.7	13.9	5.2	37.4
Polymer	A	B	C	-	-	D	E	F	G
Cis-1,4 bond content (%)	94.72	91.74	93.51	n/a	n/a	n/a	93.92	n/a	92.49
Trans-1,4 bond content (%)	4.34	6.57	5.19	n/a	n/a	n/a	4.17	n/a	7.18
Vinyl bond content (%)	0.94	1.69	1.30	n/a	n/a	n/a	1.91	n/a	0.33
Mn (kg/mol), PS	194.1	197.8	195.6	n/a	n/a	n/a	245.8	n/a	199.6
Mw/Mn	7.46	7.33	7.57	n/a	n/a	n/a	9.71	n/a	9.70

(Summary)

As seen from the above table, the polymers described in the Examples 36, 29 and 40 of US 4,429,089 (Pedretti et al.) have a cis-1,4 bond content as measured by a Fourier transform infrared spectroscopy (FT-IR) of less than 98.0%, a vinyl bond content of more than 0.3% and a ratio (Mw/Mn) of weight average molecular weight (Mw) to number average molecular weight (Mn) of more than 3.5. And no polymer can be obtained by procedure described in the Example 26.

As seen from these results, it is confirmed that US 4,429,089 (Pedretti et al.) does not disclose or suggest the butadiene-based polymer having the 1,3-butadiene monomer unit, characterized in that the cis-1,4 bond content and the vinyl bond content in the 1,3-butadiene monomer unit as measured by the Fourier transform infrared spectroscopy (FT-IR) are not less than 98.0% and not more than 0.3%, respectively, and the ratio (Mw/Mn) of the weight average molecular weight (Mw) to the number average molecular weight (Mn) is 1.6-3.5.

I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under § 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: 3-27-2009

Declarant: 

Eiju Suzuki